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Theories of the mechanical, vibrational, and electronic properties of III-V semiconductors have been developed and applied to (i) help determine the feasibility of InN-based visible and ultraviolet lasers and light detectors, (ii) develop a theory of phonons in semiconductor alloys, (iii) understand surface reconstruction of semiconductors, (iv) predict the effects of atomic correlations on the light-scattering (Raman) properties of semiconductive alloys, (v) develop a new first principles pseudofunction implementation of local-density theory, (vi) study the oxidation of GaAs, (vii) develop a theory of scanning tunneling microscope images, and (viii) understand the electronic and optical properties of highly strained artificial semiconductors and small semiconductor particles.

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PRINCIPAL INVESTIGATOR: John D. Dow

1. SUMMARY

Theories of the mechanical, vibrational, and electronic properties of III-V semiconductors have been developed and applied to (i) help determine the feasibility of InN-based visible and ultraviolet lasers and light detectors, (ii) develop a theory of phonons in semiconductive alloys, (iii) understand surface reconstruction of semiconductors, (iv) predict the effects of atomic correlations on the light-scattering (Raman) properties of semiconductive alloys, (v) develop a new first principles pseudofunction implementation of local-density theory, (vi) study the oxidation of GaAs, (vii) develop a theory of scanning tunneling microscope images, and (viii) understand the electronic and optical properties of highly strained artificial semiconductors and small semiconductor particles.

2. OBJECTIVES

Our goal is to develop theories of the mechanical, vibrational, and thermal properties of III-V semiconductor alloys that will lead to a better understanding of the physics of these materials.

3. STATUS OF RESEARCH

We have made progress on the following problems:

A. Phonons in alloys and alloy superlattices

We have calculated various combinations of the phonon densities of states, local densities of states, spectral densities, and Raman spectra for a variety of electronic materials, such as $Ga_{1-x}In_xAs$, metastable $(GaAs)_{1-x}Ge_{2x}$ [192], $Hg_{1-x}Cd_xTe$ [181][212], and superlattices.

We believe that we have all of the essential elements in hand for calculating the vibrational properties of alloys, in the case of short-ranged forces, and we are moving to extend our results to long-ranged forces. Specifically, we have abandoned the coherent potential approximation (CPA) which is analytically beautiful but fails to account properly for pair and higher correlations. Instead we have embraced the Recursion Method, which is more numerical, and we have written a vectorized version of it on our Convex computer which can execute cluster calculations for clusters large enough to represent the bulk adequately, even for long wavelength phonons. An added advantage of the Recursion Method is that it accepts any kind of cluster as input, so that it is not necessary to construct different theories for different atomic correlations (such as random alloy, chalcopyrite structure, various superlattices, etc.). Therefore, the problem of evaluating phonon spectra has been decoupled from the problem of determining atomic correlations.

To determine correlations, we have developed a Monte Carlo Ising Model scheme, simulating atomic occupations of a given site by spin projections, with the "exchange" integrals being related to the formation energies of the various combinations of bonds [207]. Hence, if we are given measured pair correlations from EXAFS, for example, we can adjust the strengths of the "exchange integrals" and "magnetic fields" in the Ising model until the observed pair correlations are obtained. At that point we have a semi-empirical Hamiltonian from which we can calculate all correlations and determine statistically typical clusters. Having done this, we can pipe the clusters into the Recursion Method and evaluate the relevant spectra.

This approach to correlated alloys is generally valid, and may be used for all ordered and disordered semiconductor alloys. It omits two features important in real materials: (i) long-ranged forces and (ii) strains due to the fact that all atoms do not occupy perfect-lattice sites. We are currently examining schemes combining the Recursion Method for short-ranged forces with Virtual Crystal and CPA methods for long-ranged forces to account properly for long-ranged forces. And we have made progress on the strain problem both in ordered alloys [227] and in predicting Type II to Type I transitions induced by strains in superlattices. These results will soon be incorporated into the phonon spectral calculations.

Some especially notable qualitative conclusions have emerged from these calculations. One is the demonstration that phonon wavefuctions are not highly localized, as recently proposed [P. Parayanthal and F. H. Pollak, Phys. Rev. Lett. 52, 1811 (1984)], a theoretical result supported by the recent Raman measurements of J. A. Kash [Bull. Amer. Phys. Soc. 33, 643 (1988)]. Another is the identification of "alloy modes" in materials such as $Hg_{1-x}Cd_xTe$ [P. M. Amirtharaj, K. K. Tiong, P. Parayanthal, F. H. Pollak, and J. K. Furdyna, J. Vac. Sci. Technol. A3, 226 (1985)] with vibrations of specific clusters involving, for example, both Hg and Cd [181]. Yet another result is the ability to identify antisite defects (at sufficient concentration) in metastable material such as $(GaSb)_{1-x}Ge_{2x}$ [186][191].

Future work will deal with phonons at surfaces, the effects of strain, and long-ranged forces.

B. Electronic properties of alloys

We have studied the electronic structure of $Pb_{1-x}Sn_xTe$ alloys [180] and found that large portions of the electronic structure are adequately approximated by the virtual crystal approximation, while some spectral features (especially low in the valence band, near the cation-derived s-states) show persistent character and require a more sophisticated theory, namely the Recursion Method. This theory produces band broadening, energy shifts, and Dimmock's band-crossing phenomenon.

C. Electronic structures and doping of InN, $In_xGa_{1-x}N$, and $In_xAl_{1-x}N$

We have predicted the electronic structures of InN, $In_xGa_{1-x}N$, and $In_xAl_{1-x}N$, and these materials have been found to be direct-gap semiconductors with fundamental band gaps ranging from orange through the blue-green to the ultraviolet (i.e., potential UV sensors). The deep levels associated with

substitutional s- and p-bonded impurities have been predicted, and, for InN we found (i) that the native defect responsible for naturally occurring n-type InN is a nitrogen vacancy (not N_{In}); (ii) that the nitrogen vacancy also produces a deep level just below the conduction band edge, which is responsible for an observed 0.2 eV optical absorption feature; (iii) that p-type doping should be achievable by inserting Column-II impurities on In sites; (iv) that n-type conductivity should result from oxygen atoms on N sites; (v) that In_N produces s- and p-like deep levels near mid-gap that are responsible for an optical absorption feature near 1 eV; (vi) that Column-IV impurities on either anion or cation sites will tend to make the material semi-insulating, and (vii) an isoelectronic electron trap should be produced by B_{In}, whereas Column-V impurities on the N site should produce deep isoelectronic hole traps. Similar results hold for the alloys $In_xGa_{1-x}N$ and $In_xA\ell_{1-x}N$. Some impurities undergo shallow-deep transitions in the alloys, as functions of alloy composition.

D. Electronic structures of uniaxial-stressed Si/Ge [111] strained-layer superlattices

We have predicted the electronic structures of Si/Ge [111] superlattices [218], including the effects of both internal strain due to lattice-mismatch and externally applied [111] uniaxial stress. In a $N_{Si}\times N_{Ge}$ Si/Ge [111] superlattice, the Ge conduction band minimum at $L=(\pi/a_{Ge})(1,1,1)$ can be folded to the zone center with suitable choices of N_{Si} and N_{Ge}, permitting the crystal momentum selection-rule for luminescence to be satisfied for the folded (1,1,1) minimum in the superlattice. However, internal strains raise the energy of the folded (1,1,1) conduction band minimum relative to the unfolded L-minima at (1,-1,-1), (-1,1,-1), and (-1,-1,1), causing the unfolded minima to be the lowest-energy conduction band states into which injected electrons thermalize -- and reinstating the selection rules against luminescence. However, application of a [111] uniaxial stress of sufficient magnitude will overcome the internal strain, will make the folded (1,1,1) L-minimum (which has significant s-character) the lowest-energy conduction band minimum, and will cause the Ge quantum wells in the superlattice to luminesce. These results also hold when the electronic structure of the superlattice is evaluated properly, rather than estimated by the zone-folding approximation.

E. Effects of strain on superlattices and ordering in alloys

We have evaluated the effects of strain on both superlattices [243] and alloys [224]. In the superlattice work we have shown that a $(ZnSe)_N(ZnTe)_M$ superlattice is Type II for N>1, but for N=1 and M<6 there is a strain-induced Type II to Type I superlattice transition. This result, we hope, will explain the strange optical properties of these interesting materials with band gaps in the blue-green portion of the spectrum.

In the alloy work, we have shown, using local density theory, that charge transfer from cation to anion in II-VI alloys is not a dominant factor in determining the local bond lengths (as measured with EXAFS) in the alloys. Then, in collaboration with Prof. K. E. Newman and her students, we have developed a theory of strain effects on alloy bond lengths which successfully describes EXAFS data.

F. Unrestricted pseudofunction theory

We have developed a spin-unrestricted local-density pseudofunction theory [168][197][200][222][226][234][242] which provides a new understanding of photoemission and inverse photoemission data for $Cd_{1-x}Mn_xTe$ alloys. We believe that with this a priori theory we can successfully predict magnetic properties of solids, and are presently studying FeTe, high-T_c superconductors, and diluted magnetic semiconductors with it.

G. Pseudofunction theory of surfaces

We have studied the surface reconstructions of zincblende and wurtzite semiconductors, and shown that ionic forces inhibit relaxation of the zincblende (110) surface [168][197][234][200] and the wurtzite (10$\bar{1}$0) surface [197]. These results involve a tour de force calculation, in which we minimize the surface free energy using local-density theory. They have also caused a bit of controversy, because previous theories neglected the ionic forces!

H. Large-gap semiconductors

We have executed calculations of the electronic structures of several large-gap semiconductors using local-density pseudopotential methods. These include diamond, BN, and the 3C, 2H, 4H, and 6H polytypes of SiC.

I. Oxidation of the GaAs (110) surface

Pseudofunction calculations [226] of (i) total energy, (ii) local spectral density of occupied states, and (iii) surface Fermi level relative to the valence band maximum for the heavily oxygenated GaAs (110) surface have been executed for several different models of the oxygen adsorption. Based on these calculations and comparison with photoemission spectra and scanning tunneling microscopy images, we conclude that at modest (half-monolayer) to heavy (monolayer) coverages the oxygen lies within the surface plane, is atomic, is bonded to several atoms, and very likely occupies more than one inequivalent site. The surface dipole layer of the oxygenated surface is nearly zero.

J. Electronic structures of small particles

We have developed a theory of small semiconductor particles [232] which naturally obtains the large-particle limit. These particles have applications in catalysis and non-linear optical storage media.

K. Theory of scanning tunneling microscopy

We have predicted the scanning tunneling microscopy images of relaxed III-V (110) surfaces with antisite defects. Surprisingly, the qualitative features of the images depend critically on the distance of the tip from the surface, and the antisite defects are virtually unrecognizable unless the bias of the tip includes the energy level of the antisite defect. These results should cause the reinterpretation of many data.

L. Structure-modulated superlattices

We have developed a theory of zincblende/wurtzite superlattices [233]

made from a single material such as CdS. In these superlattices, the periodic-disorder is topological, not compositional. Efforts to grow these superlattices are now in progress in Europe.

M. Resonant tunneling in small band-gap superlattices

We have developed a theory of resonant tunneling in small band gap semiconductors [205] which accounts for the mixing of the valence bands with the conduction bands. In some cases, the conduction band tunneling characteristics can be dominated by the light-hole valence band. Different tunneling behavior is to be expected for Type-I, Type-II and Type-III heterostructures.

N. Schemes for controllable doping of II-VI semiconductors

We have shown [239] how the strain in a superlattice can be manipulated (by selecting appropriate layer thicknesses) to drive moderately deep acceptors shallow and overcome the tendency of II-VI semiconductors in particular to resist p-doping.

We have also predicted the electronic structures of s- and p-bonded substitutional impurities in ZnSe and ZnTe, and identified the antisite defects Zn_{Te} and Li_{Te} as likely responsible for ZnTe's unique tendency among the II-VI's to be dopable p-type.

O. Deep levels and core excitons in strained superlattices

We have developed the first theories [225][228][243] of deep levels in [001] and [111] unstrained and strained superlattices, and have predicted numerous shallow-deep impurity transitions. We have also developed the first theory of core excitons in superlattices [243].

P. Effects of correlations on the Raman spectra of alloysWe have developed a theory techniques to predict the spectra of correlated alloys [207].

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232. W. M. Hu and J. D. Dow. Charge density distributions and scanning tunneling microscope images of the relaxed (110) GaAs surface with antisite defects. In preparation.

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5. PROFESSIONAL PERSONNEL

J. Dow, principal investigator
S. Ren, visiting professor
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J. Shen, graduate student
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G. Yang, graduate student
Y. Liang, graduate student
R. Wang, graduate student
D. Vasquez, graduate student
L. Lewandowski, graduate student

6. INTERACTIONS

The principal investigator has functioned as an advisor to the National Academy of Science Committee on Basic Research on a wide range of topics in materials science, electronics, and solid state physics, and to the Air Force (Capt. K. Malloy) on matters related to semiconductor alloys.

PATENTS

None.